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**(54) Title:** SILICONE COMPOSITIONS CONTAINING A SILICONE-UREA SEGMENTED COPOLYMER

**(57) Abstract**

A composition that includes: (a) a silicone fluid; (b) a silicone-urea segmented copolymer; and (c) no more than about 30 % by weight of a silicate resin.

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## SILICONE COMPOSITIONS CONTAINING A SILICONE-UREA SEGMENTED COPOLYMER

### Background of the Invention

5 This invention relates to silicone-containing compositions, and methods for preparing such compositions.

Silicone-containing compositions find application in a variety of areas. For example, when compounded with tackifiers they may be used as pressure sensitive adhesives. Moisture-curable silicone sealant compositions in the form of thixotropic 10 pastes have been used as sealants.

### Summary of the Invention

In a first aspect, the invention features a composition that includes (a) a 15 silicone fluid; (b) a silicone-urea segmented copolymer; and (c) no more than about 30% by weight of a silicate resin.

In preferred embodiments, the composition includes at least about 30% by weight of the silicone fluid and up to about 70% by weight of the silicone-urea copolymer. Particularly preferred are composition containing up to about 25% by weight of the silicone-urea copolymer.

20 The composition may be curable, e.g., by virtue of including a curable silicone fluid, a curable silicone-urea copolymer, or a combination thereof. By "curable," it is meant that the composition is capable of being crosslinked by exposure to moisture, heat, or non-ionizing radiation (e.g., ultraviolet or visible radiation). For example, the silicone fluid, the silicone-urea copolymer, or both, may contain curable 25 groups such as ethylenically unsaturated groups (in which case the composition may be cured by exposure to non-ionizing radiation or heat) or hydroxy groups (in which case the composition is moisture-curable). Separate crosslinking agents (e.g., silanes, functional siloxanes) may also be added to yield a curable composition.

30 Examples of suitable silicone fluids include both curable silicone fluids (e.g., moisture-curable silicone fluids such as hydroxy-terminated polydiorganosiloxane fluids) and substantially non-curable silicone fluids. Examples of suitable silicone-urea

copolymers include polydiorganosiloxane polyurea segmented copolymers having a degree of polymerization of at least 10, and polydiorganosiloxane-oligourethane segmented copolymers having terminal groups selected from the group consisting of functional end groups and non-functional end groups, and a degree of polymerization less than 10. As 5 used herein, "degree of polymerization" refers to the number of silicone amine units in the copolymer.

In some preferred embodiments, the composition is essentially free of silicate resin. The composition may be tacky and self-supporting at room temperature prior to curing, and may be provided in the form of a ribbon, rope, or sheet; such 10 compositions are particularly useful as sealants. A "tacky" composition is a composition which passes the Tack Test described infra. A "self-supporting" composition is a composition which passes the Stretch Test described infra.

"Polyamine" refers to polydiorganosiloxane diamine or a mixture of polydiorganosiloxane diamine and at least one organic polyamine.

15 In a second aspect, the invention features a composition that includes: (a) a silicone fluid; and (b) a polydiorganosiloxane-oligourethane segmented copolymer having terminal groups selected from the group consisting of functional end groups and non-functional end groups, and a degree of polymerization less than 10. Such compositions may, if desired, contain silicate resin, with the amount of silicate resin being selected 20 based upon the intended use of the composition.

In a third aspect, the invention features a curable composition comprising a curable silicone fluid and a silicone-urea segmented copolymer.

25 In a fourth aspect, the invention features a method for preparing a polymeric composition that includes the steps of providing a reaction mixture that includes a polyisocyanate, a polydiorganosiloxane diamine, and a silicone fluid; and reacting the polyisocyanate and the diamine with each other in the presence of the silicone fluid to produce a polymeric composition that includes the silicone fluid and a silicone-urea segmented copolymer.

In preferred embodiments, the reaction mixture is substantially solvent-free. 30 It may further include a silicate resin.

The polymeric composition may be a curable reaction mixture; for example, it may be prepared from a reaction mixture that includes a crosslinking agent.

According to one preferred embodiment, the polyisocyanate and the polyamine, and the conditions under which they are reacted, are selected to yield a 5 polydiorganosiloxane polyurea segmented copolymer having a degree of polymerization of at least 10. According to another preferred embodiment, the polyisocyanate and the polyamine, and the conditions under which they are reacted, are selected to yield a polydiorganosiloxane oligourethane segmented copolymer having terminal groups selected from the group consisting of functional end groups and non-functional end groups, and a degree of polymerization less than 10. 10

In a fifth aspect, the invention features a method for preparing a polymeric composition that includes the steps of reacting a polyisocyanate and a polyamine in the absence of solvent, to form a polydiorganosiloxane segmented copolymer; and combining the copolymer with a silicone fluid to form a polymeric composition.

15 The invention provides compositions in which physical properties such as rheology and tensile strength can be tailored to meet the needs of a specific application. As a result, a wide variety of compositions can be prepared, including pressure sensitive adhesives, self-supporting adhesives and sealants, moldable articles, potting compounds, and silicone compounds possessing tailorable green strength. If desired 20 (e.g., for enhanced thermal stability or cohesive strength), the compositions can be designed such that they are curable.

The compositions of the present invention can be prepared to exhibit novel controlled flow and handleability properties in the uncured state, being liquid-like or semi-solid at ambient temperatures. These properties can be optimized for a particular 25 application by the appropriate selection of the polyisocyanates, the molecular weights of the polyamines, the type of organic polyamines, the amount of silicone urea in the overall composition, and the presence of fillers and other additives.

The compositions of the present invention have the ability to be extruded or otherwise formed into thick constructions, into patterned shapes, or into irregularly 30 shaped surfaces. Other features and advantages of the invention will be apparent from the following description of the preferred embodiments thereof, and from the claims.

Detailed Description

Silicone compositions according to the invention include, at a minimum, a silicone fluid and a silicone-urea segmented copolymer. The relative amounts of these components in a given composition depend upon the particular rheological and mechanical properties sought, as well as the individual components themselves (e.g., molecular weight of the silicone fluid and degree of polymerization of the silicone-urea copolymer). In general, however, preferred compositions contain at least about 30% by weight of the silicone fluid and no more than about 70% by weight of the copolymer.

Silicone Fluid

The silicone fluid may be curable (through incorporation of suitable functional groups such as hydroxyl groups or ethylenically unsaturated groups, e.g., acrylate groups) or substantially non-curable. Particularly preferred are moisture-curable silicone fluids, e.g., hydroxy-terminated polydiorganosiloxanes. Any of the hydroxy-terminated polydiorganosiloxanes typically used in known silicone sealing and adhesive compositions may be used in the compositions according to the invention. One class of suitable materials includes polydiorganosiloxanes having viscosities at 25°C ranging from about 8 m<sup>2</sup>/s to about 30 m<sup>2</sup>/s. Examples of commercially available polydiorganosiloxanes falling within this class include those available from PPG Industries, Inc. under the designations Masil™ SFR 80,000, SFR 150,000, and SFR 300,000, and those available from Huls America of Piscataway, NJ under the designation PS348.7. Polydiorganosiloxanes having lower viscosities may also be used.

25

Silicone-Urea Copolymer

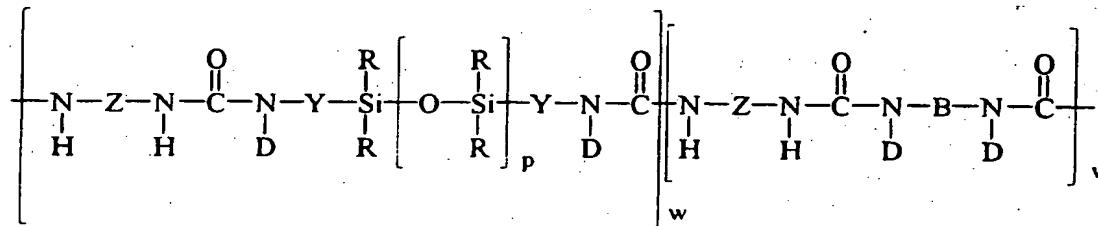
The silicone-urea copolymer is the reaction product of a polyisocyanate and a polyamine (e.g., a polydiorganosiloxane diamine). The physical properties of the composition can be tailored by adjusting the components, and amounts thereof, used to make the copolymer. In general, it is preferred to use copolymers that are substantially compatible with the silicone fluid. For example, it is preferred to use alkyl group

containing copolymers in combination with alkyl group containing silicone fluids, aromatic group containing copolymers in combination with aromatic group containing silicone fluids, etc.

One variable influencing the physical properties of the composition is the 5 degree of polymerization (DP) of the copolymer. This factor affects not only the ultimate viscosity of the composition, but the rate at which the viscosity builds during processing. In general, the higher the degree of polymerization, the more pronounced the effect of the copolymer on viscosity. One way of adjusting the degree of polymerization is by adjusting the ratio of isocyanate groups to reactive end groups 10 (e.g., amine groups) on the siloxane.

One class of suitable copolymers includes polydiorganosiloxane-polyurea segmented copolymers having a degree of polymerization of at least 10. Such copolymers can be represented by the repeating unit

15



20 wherein:

each R is a moiety that, independently, is an alkyl moiety (preferably having about 1 to about 12 carbon atoms) and may be substituted with, for example, trifluoroalkyl or vinyl groups, a vinyl radical, or higher alkenyl radical, preferably represented by the formula  $\text{R}^2(\text{CH}_2)_a\text{CH}=\text{CH}_2$  wherein  $\text{R}^2$  is  $-(\text{CH}_2)_b-$  or  $-(\text{CH}_2)_c\text{CH}=\text{CH}-$  and a is 1, 2, or 3; b is 0, 3, or 6; and c is 3, 4, or 5, a cycloalkyl moiety having about 6 to 12 carbon atoms and may be substituted with alkyl, fluoroalkyl, and vinyl groups, or an aryl moiety preferably having about 6 to 20 carbon atoms and may be substituted with, for example, alkyl, fluoroalkyl, and

vinyl groups, or an aryl moiety preferably having about 6 to 20 carbon atoms and may be substituted with, for example, alkyl, cycloalkyl, fluoroalkyl, and vinyl groups, or R is a perfluoroalkyl group as described in U.S. Pat. No. 5,028,679 (hereby incorporated by reference), or a perfluoroether-containing group as

5 described in U.S. Pat. Nos. 4,900,474 and 5,118,775 (hereby incorporated by reference); preferably at least 50% of the R moieties are methyl radicals, with the balance being monovalent alkyl or substituted alkyl radicals having 1 to 12 carbon atoms, alkenylene radicals, phenyl radicals, or substituted phenyl radicals;

each Z is a polyvalent radical selected from arylene radicals and

10 aralkylene radicals preferably having from about 6 to 20 carbon atoms, alkylene and cycloalkylene radicals preferably having from about 6 to 20 carbon atoms, preferably Z is 2,6-tolylene, 4,4'-methylenediphenylene, 3,3'-dimethoxy-4,4'-biphenylene, tetramethyl-*m*-xylylene, 4,4'-methylenedicyclohexylene, 3,5,5-trimethyl-3-methylenecyclohexylene, 2,2,4-trimethylhexylene, 1,6-hexamethylene, 15 1,4-cyclohexylene, and mixtures thereof;

each Y is a polyvalent radical that is an alkylene radical of 1 to 10 carbon atoms, an aralkylene radical, or an arylene radical (preferably having 6 to 20 carbon atoms);

each D is selected from the group consisting of hydrogen, an alkyl

20 radical of 1 to 10 carbon atoms, and phenyl;

B is a polyvalent radical selected from the group consisting of alkylene, aralkylene, cycloalkylene, phenylene, polyalkylene oxide, including for example, polyethylene oxide, polypropylene oxide, polytetramethylene oxide, and copolymers and mixtures thereof;

25 v is a number that is 0 to about 1000;

w is a number that is greater than or equal to 1; and

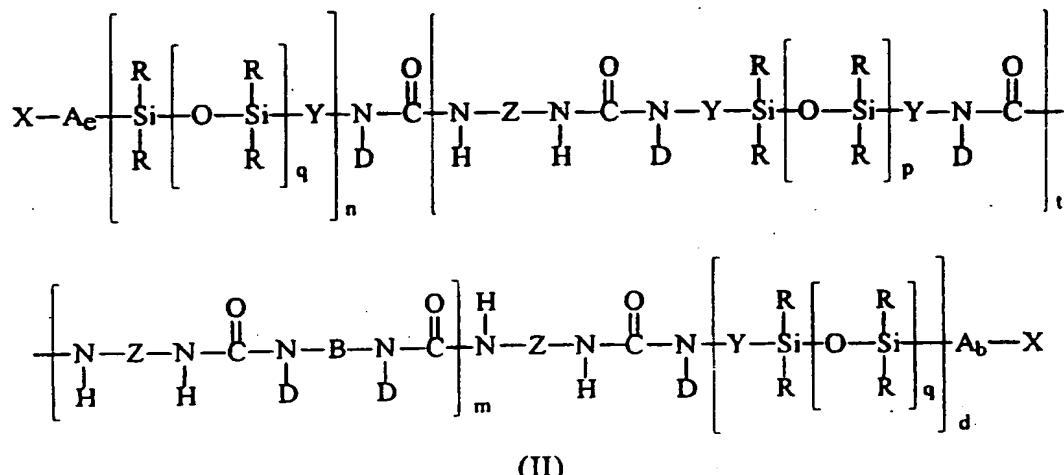
p is a number that is about 10 or larger, preferably about 15 to 2000, more preferably about 30 to 1500.

A second class of suitable copolymers includes polydiorganosiloxane-

30 oligourethane segmented copolymers having terminal groups selected from the group

consisting of functional end groups and non-functional end groups, and a degree of polymerization less than 10.

The polydiorganosiloxane oligourethane segmented copolymer compositions useful in the present invention can be represented by Formula II



5

wherein, Z, D, Y, R, B and p are defined as above;

each A is independently -B-, or -YSi(R)<sub>2</sub>(OSi(R)<sub>2</sub>)<sub>p</sub>Y- or mixtures thereof;

m is a number that is 0 to about 8;

10 b, e, d and n are 0 or 1, with the provisos that, b+d = 1 and e+n = 1;

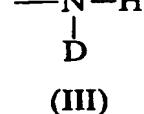
q is about 10 or larger, preferably about 15 to 2000, more preferably about 30 to 1500; and

t is a number which is 0 to about 8;

15

each X is independently:

(a) a moiety represented by

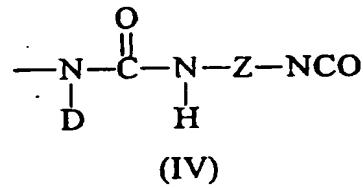


(III)

20

wherein D is defined as above;

(b) a moiety represented by

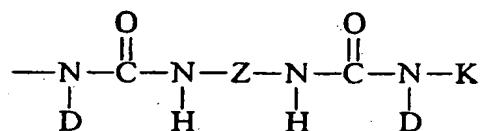


(IV)

where each of D and Z are defined as above,

(c) a monovalent moiety that is not reactive under moisture curing or free radical curing conditions and that can be the same or different and that are alkyl moieties preferably having about 1 to 20 carbon atoms and that can be 5 substituted with, for example, trifluoroalkyl groups, or aryl moieties preferably having about 6 to 20 carbon atoms and that may be substituted with, for example alkyl, aryl, and substituted aryl groups;

(d) a moiety represented by



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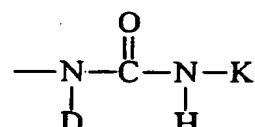
(V)

where each of Z, and D are defined as above,

K is independently (i) a moiety that is not reactive under moisture curing or free radical curing conditions and that can be the same or different 15. selected from the group consisting of alkyl, substituted alkyl, aryl, and substituted aryl; (ii) a non-ionizing radiation or heat curable ethylenically unsaturated end group such as acrylate, methacrylate, acrylamido, methacrylamido and vinyl groups; (iii) a moisture curable group such as, for example, alkoxy silane and oxime silane groups; and

20

(e) a moiety represented by

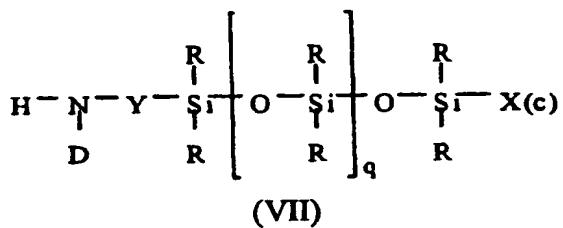


(VI)

wherein D, and K are defined as above.

25

Polydiorganosiloxane monoamines useful in the present invention as end capping agents can be represented by the formula



where D, R, X(c), Y and q are as defined above, and include those  
5 having number average molecular weights in the range of about 700 to 150,000. Preferred are polydiorganosiloxane monoamines prepared as described in U.S. Pat. No. 5,091,483. The polydiorganosiloxane monoamines can be prepared, for example, from the reaction of cyclic organotrisiloxanes with alkyl lithium reagents in tetrahydrofuran to yield lithium polydiorganosiloxanates that are subsequently reacted with aminoalkylfluorosilanes as terminating agents to provide the  
10 polydiorganosiloxane monoamine product.

Examples of polydiorganosiloxane monoamines useful in the present invention include polydimethylsiloxane monoamine, polydiphenylsiloxane monoamine, polytrifluoropropylmethylsiloxane monoamine, 15 polyphenylmethylsiloxane monoamine, polydiethylsiloxane monoamine, polydivinylsiloxane monoamine, polyoxyalkylene oxide, polyvinylmethylsiloxane monoamine, and copolymers thereof and mixtures thereof.

Suitable endcapping agents for polydiorganosiloxane oligourethane segmented copolymers that would be terminated with amine groups, were no endcapping agent present, and that provide terminal groups that are not reactive under moisture curing or free radical curing conditions, include monoisocyanates such as alkyl isocyanates, such as benzyl isocyanate, cyclohexyl isocyanate, n-dodecyl isocyanate, n-octadecyl isocyanate, octyl isocyanate, 2-phenylethyl isocyanate, trimethylsilyl isocyanate, undecyl isocyanate; and aryl isocyanates, such as 4-bromophenyl isocyanate, 2-chlorophenyl isocyanate, 2,4-dimethylphenyl isocyanate, 1-naphthyl isocyanate, phenyl isocyanate, 4-tolyl isocyanate, 4-trifluoromethylphenyl isocyanate, 2,4,6-trimethylphenyl isocyanate.

## Suitable endcapping agents for polydiorganosiloxane oligourethane segmented copolymers that would be terminated with isocyanate groups, were no

endcapping agent present, and provide terminal groups that are not reactive under moisture curing or free radical curing conditions, include monoamines such as propylamine, cyclohexylamine, aniline, benzylamine, octadecylamine, phenylethylamine and polyoxyalkylene, such as those that can be obtained from

5 Huntsman, Corp. under the trade name of Jeffamine, polyethylene oxide, polypropylene oxide, copolymers thereof and mixtures thereof.

Suitable endcapping agents for polydiorganosiloxane oligourea segmented copolymers that would be terminated with amine groups, were no endcapping agent present, and that provide terminal groups that are reactive under

10 free radical curing conditions, include isocyanatoethyl methacrylate; alkenyl azlactones such as vinyl dimethyl azlactone and isopropenyl dimethyl azlactone, m-isopropenyl- $\alpha,\alpha$ -dimethyl benzyl isocyanate, and acryloyl ethyl carbonic anhydride. Some endcapping agents that can react with amine groups, e.g., isocyanatoethyl methacrylate, are commercially available, and others can be prepared using known

15 methods. Alkenyl azlactones and their preparations are described, for example, in U.S. Pat. No. 4,777,276, wherein such description is incorporated herein by reference. Acryloyl ethyl carbonic anhydride can be prepared from ethyl chloroformate and acrylic acid as described in R. Hatada et al., *Bull. Chem. Soc. Japan*, 41 (10), 2521 (1968). Preferred endcapping agents for

20 polydiorganosiloxane oligourea segmented copolymers that would be amine terminated if no endcapping agent were present include, for example, isocyanatoethyl methacrylate, vinyl dimethyl azlactone, and acryloyl ethyl carbonic anhydride.

Suitable endcapping agents for polydiorganosiloxane oligourea

25 segmented copolymers that would be amine terminated, if no endcapping agent were present, to provide terminal groups that are reactive under moisture curing conditions include isocyanatopropyl trimethoxysilane, isocyanatopropyl triethoxysilane, isocyanatopropyl dimethoxy (methylethylketoximino)silane, isocyanatopropyl diethoxy (methylethylketoximino)silane, isocyanatopropyl

30 monomethoxy di(methylethylketoximino)silane, isocyanatopropyl monoethoxy di(methylethylketoximino)silane, and isocyanatopropyl

tri(methylethylketoximino)silane. Polyisocyanates that serve to form the copolymer, may also serve as the moisture curable terminal portion of the copolymer when the number of isocyanate groups provided by the polyisocyanates exceed the amine groups provided by the polyamines. Polymers prepared with 5 such end-capping agents can be further reacted to provide higher molecular weight polymers or copolymers.

Suitable endcapping agents for polydiorganosiloxane oligourethane segmented copolymers that would be isocyanate terminated if no endcapping agent were present to provide terminal groups that are reactive under moisture curing 10 conditions include aminopropyl trimethoxysilane, aminopropyl triethoxysilane, aminopropyl methyldimethoxysilane, aminopropyl methyldiethoxysilane, aminopropyl dimethoxy(methylethylketoximino)silane, aminopropyl diethoxy(methylethylketoximino)silane, aminopropyl monomethoxydi(methylethylketoximino)silane, aminopropyl 15 monoethoxydi(methylethylketoximino)silane, and aminopropyl tri(methylethylketoximino)silane. Preferred endcapping agents, for isocyanate-terminated polydiorganosiloxane polyurea segmented oligomers, if no end-capping agents were present to provide terminal groups that are reactive under various conditions, include those selected from the group consisting of aminopropyl 20 trimethoxysilane, aminopropyl triethoxysilane and aminopropyl methyldiethoxysilane.

As in the case of the first group of copolymers, these copolymers may be provided with one or more curable groups in the case of curable compositions.

The molecular weight of the silicone amine used to prepare the 25 copolymers can also be varied in order to produce a composition having a defined set of properties. In general, the lower the molecular weight of this reactant, the higher the viscosity (and thus the stiffness) of the composition. Preferably, the molecular weight can be in the range from about 5,000 to about 100,000, with molecular weights in the range 15,000 to 100,000 being preferred.

30 Suitable polydiorganosiloxane diamines are disclosed, for example, in U.S. Pat. No. 3,890,269 (Martin); U.S. Pat. No. 4,661,577 (Lane et al.); U.S. Pat.

No. 5,026,890 (Webb et al.); U.S. Pat. No. 5,276,122 (Aoki et al.), as well as International Patent Publication No. WO 95/03354. Polydiorganosiloxane diamines are commercially available from, e.g., Shin-Etsu Silicones of America, Inc., Torrance, CA, and Huls America, Inc. Particularly preferred are substantially 5 pure polydiorganosiloxane diamines prepared as disclosed in U.S. Pat. No. 5,214,119 (Leir et al.). Specific examples of useful polydiorganosiloxane diamines include polydimethylsiloxane diamine, polydiphenylsiloxane diamine, polytrifluoropropylmethylsiloxane diamine, polyphenylmethylsiloxane diamine, polydiethylsiloxane diamine, polydivinylsiloxane diamine, polyvinylmethylsiloxane 10 diamine, poly(5-hexenyl)methylsiloxane diamine, copolymers thereof, and mixtures thereof.

The choice of polyisocyanate also affects the physical properties of the polymeric composition. For example, the polyisocyanate may affect the hydrogen bonding capability of the copolymer (and thus the stiffness of the composition). In 15 general, stronger hydrogen bonding results in higher viscosity (and thus higher stiffness).

Any polyisocyanate capable of reacting with the above-described polyamine or monoamine reactants can be used. Examples of suitable polyisocyanates include:

20 (1) aromatic diisocyanates such as 2,6-toluene diisocyanate; 2,5-toluene diisocyanate; 2,4-toluene diisocyanate; m-phenylene diisocyanate; p-phenylene diisocyanate; methylene bis(o-chlorophenyl diisocyanate); methylenediphenylene-4,4'-diisocyanate; polycarbodiimide-modified methylenediphenylene diisocyanate; (4,4'-diisocyanato-3,3',5,5'-tetraethyl) diphenylmethane; 4,4'-diisocyanato-3,3'-dimethoxybiphenyl (o-dianisidine diisocyanate), 5-chloro-2,4-toluene diisocyanate, and 1-chloromethyl-2,4-diisocyanato benzene;

25 (2) aromatic-aliphatic diisocyanates such as m-xylylene diisocyanate and tetramethyl-m-xylylene diisocyanate;

30 (3) aliphatic diisocyanates such as 1,4-diisocyanatobutane; 1,6-diisocyanatohexane; 1,12-diisocyanatododecane; and 2-methyl-1,5-diisocyanatopentane; and

(4) cycloaliphatic diisocyanates such as methylenedicyclohexylene-4,4'-diisocyanate; 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (isophorone diisocyanate); and cyclohexylene-1,4-diisocyanate.

5 (5) multifunctional isocyanates such as Mondur<sup>TM</sup> 489 and Desomdur<sup>TM</sup> N-3300, each commercially available from Bayer.

Particularly preferred polyisocyanates are methylenedicyclohexylene-4,4'-diisocyanate ("H<sub>12</sub>MDI") and tetramethyl-m-xylylene diisocyanate ("TMXDI"), both of which give rise to relatively strong hydrogen bonding. Other examples of suitable polyisocyanates include 1,12-diisocyanatododecane ("1,12-ddDI"), 3,3'-dimethoxy-4,4'-biphenylene diisocyanate ("dADI"), isophorone diisocyanate ("IPDI"), m-xylylene diisocyanate ("m-XDI"), and methylenediphenylene-4,4'-diisocyanate ("MDI").

10 Mono-functional isocyanates may also be included to control molecular weight.

15 Another factor which can affect the physical properties of the polymeric composition is the amount of copolymer included in the composition, with higher amounts giving rise to higher viscosities. Generally, amounts ranging up to about 70% by weight may be incorporated, with amounts up to about 25% by weight being preferred. For example, in the case of self supporting rope sealants, the 20 preferred amount of copolymer typically is about 15-20% by weight based upon the total weight of the composition.

#### Other Ingredients

25 The composition may contain other ingredients as well. For example, the composition may contain a silicate tackifying resin. Such resins are particularly useful in the case of pressure sensitive adhesive compositions. Preferably, the amount of silicate resin is no greater than about 30% by weight, although in the case of pressure sensitive adhesives it can be higher.

30 Silicate resins useful in the present invention include those composed of the structural units M, D, T, Q, and combinations thereof. For example, MQ silicate resins, MQD silicate resins, and MQT silicate resins that also

may be referred to as copolymeric silicate resins and that preferably have a number average molecular weight of about 100 to about 50,000, more preferably about 500 to about 10,000 and generally have methyl substituents. Silicate resins include both nonfunctional and functional resins, the functional resins having one or more

5 functionalities including, for example, silicon-bonded hydrogen, silicon-bonded alkenyl, and silanol. MQ silicate resins are copolymeric silicate resins having  $R'_3SiO_{1/2}$  units and  $SiO_{4/2}$  units. Such resins are described in, for example, *Encyclopedia of Polymer Science and Engineering*, vol. 15, John Wiley & Sons, New York, (1989), pp. 265-270, and U.S. Pat. No. 2,676,182, U.S. Pat. No.

10 3,627,851, U.S. Pat. No. 3,772,247, and U.S. Pat. No. 5,248,739. MQ silicate resins having functional groups are described in U.S. Pat. No. 4,774,310 that has silyl hydride groups, U.S. Pat. No. 5,262,558 that has vinyl and trifluoropropyl groups, and U.S. Pat. No. 4,707,531 that has silyl hydride and vinyl groups. The above-described resins are generally prepared in solvent. Dried, or solventless,

15 MQ silicate resins can be prepared as described in U.S. Pat. No. 5,319,040, U.S. Pat. No. 5,302,685, and U.S. Pat. No. 4,935,484. MQD silicate resins are terpolymers having  $R'_3SiO_{1/2}$  units,  $SiO_{4/2}$  units, and  $R'_2SiO_{2/2}$  units such as are taught in U.S. Pat. No. 2,736,721. MQT silicate resins are terpolymers having  $R'_3SiO_{1/2}$  units,  $SiO_{4/2}$  units and  $R'SiO_{3/2}$  units such as are taught in U.S. Pat. No.

20 5,110,890 which is incorporated herein by reference and Japanese Kokai HE 2-36234.

Commercially available silicate resins include SR-545, MQ resin in toluene, available from General Electric Co., Silicone Resins Division, Waterford, NY; MQOH resins which are MQ silicate resins in toluene, available from PCR, Inc., Gainesville, FL; MQR-32-1, MQR-32-2, and MQR-32-3 resins which are MQD resin in toluene, available from Shin-Etsu Chemical Co. Ltd., Torrance, CA; and PC-403, hydride functional MQ resin in toluene available from Rhone-Poulenc, Latex and Specialty Polymers, Rock Hill, SC. Such resins are generally supplied in organic solvent and may be employed in compositions of the present invention as received. However, these organic solutions of silicate resin may also be dried by any number of techniques known in the art, such as spray drying, oven drying,

steam drying, etc. to provide a silicate resin at about 100% nonvolatile content for use in compositions of the present invention. Also useful in compositions of the present invention are blends of two or more silicate resins.

Other ingredients which may be added include fumed silicas (preferably 5 having relatively high surface areas in the range of about 50-400 m<sup>2</sup>/g) in an amount ranging from about 0 to about 25% by weight. Suitable fumed silicas include those commercially available from Cabot Corp. of Tuscola, IL under the trade designations L-90, LM-130, LM-150, MD-7, MS-55, MS-75D, H5, M5, HS-5, EH-5, TS720, TS530, and TS610, and from Degussa Corp. of Dublin, OH 10 under the trade designations Aerosil 90, 130, 150, 200, 300, 380, R202, R810, R811, R812, R975, R972, and R974. Particularly preferred silicas are hydrophobic fumed silicas (i.e., fumed silicas provided with a hydrophobic treatment). Such silicas have a reduced tendency to absorb moisture, and thus introduce less moisture into the composition, compared to silicas lacking a hydrophobic coating; 15 exposure to moisture is undesirable because it initiates premature cure in the case of moisture-curable compositions. Also preferred are densified fumed silicas. Such silicas facilitate compounding and processing because they have higher bulk densities and are easier to feed and incorporate. Examples of densified silicas (both of which are commercially available from Degussa Corp.) include R974V (having a 20 bulk density of 120 g/l and a surface area of 170 m<sup>2</sup>/g) and R972V (a hydrophobic fumed silica having a bulk density of 120 g/l and a surface area of 110 m<sup>2</sup>/g).

In the case of curable compositions, the composition may further include one or more crosslinking agents such as silanes and functional siloxanes. The amount of crosslinker incorporated is preferably at least about 1-2.5% by 25 weight excess over the amount needed to react all of the available hydroxy-silicon groups (in the case of moisture-curable compositions). One class of crosslinking agents particularly useful in the case of moisture-curable silicone fluids includes silane crosslinking agents. Suitable silanes generally have the formula R<sub>n</sub>SiY<sub>4-n</sub> where R is a monovalent hydrocarbon group (e.g., an alkyl, alkenyl, aryl, or alkaryl group); n is 0, 1, or 2; and Y is a monovalent hetero-alkyl or aryl group such as an alkylketoxamino group (e.g., methylethylketoxamino, dimethylketoxamino, or 30 alkylketoxamino group (e.g., methylethylketoxamino, dimethylketoxamino, or

diethylketoxamino), alkoxy group (e.g., methoxy, ethoxy, or butoxy), alkenoxy group (e.g., isopropenoxy), acyl group (e.g., acetoxy), alkamido group (e.g., methacetamido or ethylacetamido), or arylamido group (e.g., benzylamido). Particularly preferred silane crosslinking agents are alkylketoaminosilanes because

5 they exhibit good shelf stability and do not form deleterious by-products upon cure. Examples include methyltris(methylethylketoxime)silane ("MOS") and vinyltris(methylethylketoxime silane ("VOS"), both of which are commercially available from Allied-Signal, Inc. of Morristown, NJ, and alkyloxsilanes available from OSi Chemicals of Danbury, CT under the designations Y11597, Y11343, and

10 A171.

Other ingredients which may be included in the composition are, for example, adhesion promoters, plasticizers, curing catalysts (in the case of curable compositions), fillers, dyes, fungicides, fire retardants, and ultraviolet stabilizers. The amounts of these ingredients are selected such that the desired properties of

15 the composition are maintained.

Examples of suitable adhesion promoters include alkoxy silanes such as methyltrimethoxysilane, vinyltrimethoxysilane, gamma-glycidoxypropylmethyldiethoxysilane, and gamma-mercaptopropyltrimethoxysilane. Suitable commercially available adhesion

20 promoters include alkoxy silanes commercially available from OSi Chemicals under the designations A1120, A1170, and Y11542.

Suitable plasticizers include polydialkyl siloxane oils which do not react with the other ingredients in the composition. Such plasticizers typically have viscosities in the range of about 0.7 to 6 m<sup>2</sup>/s and include siloxane oils

25 commercially available from Huls and PPG.

Examples of suitable curing catalysts (in the case of curable compositions) include amines, alkyl tin derivatives (e.g., dibutyltindilaurate, dibutyltindiacetate, and dibutyltindioctoate), alkyl titanates (e.g., tetraisobutylorthotitanate, titanium acetylacetone, and acetoacetic ester titanate),

30 and platinum derivatives.

Photoinitiators may also be used (in which case cure is typically effected by exposure to ultraviolet radiation). Suitable photoinitiators include benzoin ethers, benzophenone and derivatives thereof, acetophenone derivatives, camphorquinone, and the like. Photoinitiator is generally used at a concentration of from about 0.1% to about 5% by weight of the total polymerizable composition, and, if curing is carried out under an inerting fluid, the fluid is preferably saturated with the photoinitiator or photoinitiators being utilized in order to avoid the leaching of initiator from the silicone composition. The rapid cure observed for these materials allows for the use of very low levels of photoinitiator, thereby achieving a uniform cure of thick sections. If desired, the silicone compositions of this invention can also be cured thermally, requiring the use of thermal initiator such as peroxides, azo compounds, or persulfates generally at a concentration of from about 1% to about 5% by weight of the total polymerizable composition. It is preferable that any thermal or photo-initiator used be soluble in the silicone compositions themselves, requiring no use of solvent.

Other catalysts useful for moisture curable polydiorganosiloxane oligourethane segmented copolymers include acids, anhydrides, and lower alkyl ammonium salts thereof which include but are not limited to those selected from the group consisting of trichloroacetic acid, cyanoacetic acid, malonic acid, nitroacetic acid, dichloroacetic acid, difluoroacetic acid, trichloroacetic anhydride, dichloroacetic anhydride, difluoroacetic anhydride, triethylammonium trichloroacetate, trimethylammonium trichloroacetate, and mixtures thereof.

Also useful for curing compositions of this invention are the well known two component room temperature free radical curatives consisting of a polymerization catalyst and an accelerator. Common polymerization catalysts useful in this two component curative include organic peroxides and hydroperoxides such as dibenzoyl peroxide, t-butyl hydroperoxide, and cumene hydroperoxide, that are not active at room temperature in the absence of an accelerator. The accelerator component of the curative consists of the condensation reaction product of a primary or secondary amine and an aldehyde. Common accelerators of this type are butyraldehyde-aniline and butyraldehyde-

butylamine condensation products sold by E.I. duPont de Nemours & Co. as Accelerator 808™ and Accelerator 833™. This catalyst system may be employed to prepare a two-part free radically curable organosiloxane oligourethane segmented copolymer where the curable copolymer is divided into two parts and to one part is 5 added the polymerization catalyst and to the other part is added the accelerator. Upon mixing this two component system cures at room temperature. Alternatively, the polymerization catalyst can be incorporated in the free radically curable polyorganosiloxane oligourethane segmented copolymer and the accelerator can be applied to a substrate such that when the free radically curable 10 organosiloxane oligourethane segmented copolymer containing polymerization catalyst contacts the "primed" substrate surface, cure proceeds immediately at room temperature. Those of ordinary skill in the art are familiar with such cure systems and could readily adapt them to various product constructions.

Examples of suitable fillers include precipitated silica, silica aerogel, 15 ground quartz, calcium carbonate, magnesium carbonate, kaolin, talc, titanium dioxide, aluminum silicate, diatomaceous earth, ferric oxide, zinc oxide, ceramic microspheres, glass microbubbles, and fibrous fillers (e.g., glass and ceramic fibers).

20 **Manufacture**

The compositions are preferably prepared in an essentially solvent-free process whereby the silicone-urethane copolymer is generated *in situ* while blending in the silicone oil. Any reactor that can provide intimate mixing of the polyamines and polyisocyanates, the reaction products thereof, the silicone fluid, and any 25 optional reactants and additives, is suitable for use in the invention. The reaction may be carried out as a batch process using, for example, a flask equipped with a mechanical stirrer, provided the product of the reaction has a sufficiently low viscosity at the processing temperature to permit mixing, or as a continuous process using, for example, a single screw or twin screw extruder. Preferably, the 30 reactor is a wiped surface counter-rotating or co-rotating twin screw extruder.

The temperature in the reactor is preferably the minimum temperature needed to permit conveying of the materials through the reactor, and any subsequent processing equipment such as, for example, feedblocks and dies. For conveying the reacted material, the temperature should preferably be no more than 5 about 250°C, more preferably no more than about 100°C. Residence time in the reactor typically varies from about 5 seconds to 30 minutes, more typically from about 15 seconds to 15 minutes.

10 The residence time depends on several parameters, including, for example, the length to diameter ratio of the reactor, mixing rates, overall flow rates, reactants, and the need to blend in additional materials.

When a wiped surface reactor is used, relatively close clearances between the screw flight lands and the barrel are preferred. The screws utilized are preferably fully or partially intermeshing or fully or partially wiped in the zones where a substantial portion of the reactions take place.

15 Because of the rapid reaction that occurs between the polyamines and the polyisocyanates, both materials are preferably fed into an extruder at unvarying rates, particularly when using higher molecular weight polydiorganosiloxane diamines, that is, with number average molecular weights of about 20,000 and higher. Such feeding configurations generally reduce undesirable variability of the 20 final product. The feed rates of silicone fluid and any co-reactant should similarly be continuous.

25 In the case of polydiorganosiloxane polyurea segmented copolymers, one method of insuring continuous feeding when a very low flow polyisocyanate stream is used in an extruder is to allow the polyisocyanate feed line to touch or very nearly touch the passing threads of the screws. Another method would be to utilize a continuous spray injection device that produces a continuous stream of fine droplets of polyisocyanates in the reactor. A preferred method is to embed the polyisocyanate feed line in the feed stream of any fluid that is substantially non-reactive with the polyisocyanate, or otherwise combining the streams.

30 Typically, in formulating products of the present invention with additives such as tackifying resins, inorganic fillers, or other materials with the

reactants, the additives to be blended are added in any order provided the addition of an additive does not interfere with the reaction of reactants. For example, an additive that is particularly reactive with an isocyanate reactant typically would not be added until after the reaction of the isocyanate with an amine reactant. Further, 5 the reactants can be added simultaneously or sequentially into the reactor and in any sequential order, for example, the amine reactants can be the first component added into the reactor in a manner such as mentioned above. Isocyanate reactants can then be added downstream in the reactor. Alternately, the isocyanate reactants can be added after the amine reactants have been introduced into the reactor. The 10 silicone oil and optional co-reactants can similarly be added in sequences that do not interfere with obtaining the desired products.

The compositions may also be prepared in an essentially solvent-free process by adding a pre-formed polydiorganosiloxane segmented copolymer to the extruder, along with the silicone fluid and any additional ingredients. One method 15 of producing the desired composition is to first melt the copolymer pellets, then blend in the silicone oil and optional additives and reactants. Other orders of addition can be done, with the proper selection of screw speed, flowrates, and temperature profile to effect mixing.

20 **Titration of Polydiorganosiloxane Diamines**

Multiple lots of some of the diamines were synthesized for various examples. As used herein, molecular weight refers to the number average molecular weight. The number average molecular weight of polydiorganosiloxane or organic diamines were determined by the following acid titration. Sufficient 25 diamine to yield about 1 milliequivalent of amine is dissolved in 50/50 tetrahydrofuran/isopropyl alcohol to form a 10% solution. This solution was titrated with 1.0N hydrochloric acid with bromophenol blue as an indicator to determine number average molecular weight. The molecular weights are dependent on the exact ratio of the reactants used in the diamine synthesis and the 30 extent of stripping cyclic siloxanes. Remaining cyclics are diluents that increase the apparent molecular weight of polydiorganosiloxane diamine.

Preparation of Polydiorganosiloxane Diamines

A mixture of 4.32 parts bis(3-aminopropyl)tetramethyl disiloxane endblocker and 95.68 parts octamethylcyclotetrasiloxane ( $D_4$ ) was placed in a 5 batch reactor and purged with nitrogen for 20 minutes. The mixture was then heated in the reactor to 150°C. Catalyst, 100 ppm of 50% aqueous cesium hydroxide, was added and heating continued for 6 hours until the bis(3-aminopropyl) tetramethyl disiloxane had been consumed. The reaction mixture was cooled to 90°C, neutralized with excess acetic acid in the presence of some 10 triethylamine, and heated under high vacuum to remove cyclic siloxanes over a period of at least five hours. The material was cooled to ambient temperature, filtered to remove any cesium acetate that had formed, and titrated with 1.0N hydrochloric acid to determine number average molecular weight. The molecular weight of the diamine was 5,280.

15 Using this procedure, but varying the ratio of endblocker to  $D_4$ , silicone diamines with molecular weights from 5,000 to 20,000 were prepared.

In the case of polydimethylsiloxane diamine molecular weights greater than 20,000, the endblocker was substituted for 5,280 molecular weight polydimethylsiloxane diamine, and the molecular weight was controlled by the ratio 20 of  $D_4$  to 5,280 molecular weight polydimethylsiloxane diamine.

Preparation of Polydimethylsiloxane Monoamines

The following polydimethylsiloxane monoamines were synthesized for various examples according to the procedures of US 5,091,483, Example 6 25 (terminating agent) and Example 10 (silicone monoamine). The actual number average molecular weight of the different lots are determined by acid titration.

Aminopropyldimethylfluorosilane Terminating Agent

To a 500 mL 3-necked round bottom flask was added 49.6 grams 30 1,3-bis(3-aminopropyl)tetramethyldisiloxane, 29.6 grams ammonium fluoride, and 300 mL cyclohexane. While heating under reflux, water was removed by means of

Dean-Stark trap. After 18 hours, 4.4 mL of water was collected, and the clear, colorless solution was transferred while warm to a 500 mL 1-neck round bottom flask. The solvent was removed on a rotary evaporator to provide 165 grams of white solid. The solid was dissolved in 200 mL methylene chloride, 30 grams of 5 hexamethyl disilazane was added, and the mixture was stirred and heated under reflux for 5 hours. The mixture was filtered and the solvent removed under aspirator vacuum. The product was distilled (boiling point of 70°C) under aspirator vacuum to provide 3-aminopropyldimethylfluorosilane as a clear, colorless oil. The yield was 54 grams (100%), that was determined to be pure by 10 vapor phase chromatography. The structure was confirmed by NMR spectroscopy.

#### Polydimethylsiloxane Monoamine

To 1.6 parts of 2.5 M n-butyl lithium were added 7.4 parts of 15 octamethylcyclotetrasiloxane that had been purged with argon and the mixture was then stirred for 30 minutes; 500 parts of 50% hexamethylcyclotrisiloxane in dry tetrahydrofuran was added and the reaction mixture stirred at room temperature for 18 hours until the polymerization was complete. To the resulting viscous syrup was added 3.4 parts 3-aminopropyldimethyl fluorosilane terminating agent. The 20 viscosity rapidly decreased. After stirring for 2 hours, the solvent was distilled off on a rotary evaporator. The product was filtered to remove lithium fluoride and provided Polydimethylsiloxane Monoamine A as a clear, colorless oil. The number average molecular weight of the Polydimethylsiloxane Monoamine was 9800.

#### 25 Test Methods

The following test methods were used to characterize the polydiorgano-siloxane polyurea segmented copolymers produced in the following examples:

##### A. Shear Modulus and Viscosity

30 The storage  $G'(\omega)$  and loss  $G''(\omega)$  shear moduli were determined using a Rheometrics RDA II shear rheometer operated in the oscillatory mode. The

RDA II rheometer (available from Rheometrics Inc., Piscataway, NJ) was equipped with 8 mm parallel plates surrounded with a temperature programmable oven equipped with an inert gas purge. The rheometer mechanical drive assembly, parallel plates and oven were enclosed in an acrylic plastic box which further 5 isolated the test environment from fluctuations in laboratory temperature and humidity. The pouch containing the rope was opened under dry nitrogen purge, after which sufficient sealant to cover the rheometer plates was removed and placed on the rheometer base plate. The rheometer plates were engaged and the spacing between plates maintained in the range of 1.4 - 2.0 mm during 10 measurement. Tests were run at 25+/- 1°C under dry nitrogen. Shear moduli measurements were made throughout the frequency range of from 0.1 to 100 radians per second, and shear moduli are reported for the endpoints of frequency spectra, i.e., at 0.1 and 100 radians per second. In some cases the 0.1 radian per second shear modulus was so low that it caused the rheometer transducer to be out 15 of specification.

The viscosity was calculated from the storage and loss shear moduli using the following formula: viscosity ( $\eta$ ) =  $[G'(\omega)^2 + G''(\omega)^2]^{1/2}/\omega$ .

#### B. Tensile Strength and Elongation

20 Uncured compositions were pressed into films between two suitable liners (e.g., plastic sheets such as polyethylene) using a hydraulic press, to produce samples having a thickness of 2.0 mm. The test samples were then cured for 7 days at 25°C/50% relative humidity. The tensile strength and percent elongation of the cured test sample were then measured according to ASTM D412, using die C.

25

#### C. Stretch

The foil pouch containing the rope was peeled open by pulling the top and bottom portions of the pouch apart to expose the entire length of rope. The sides of the bottom portion of the opened pouch were then taped to the surface of 30 the table such that the entire interior of the pouch, as well as the rope, was exposed. Next, a 15 cm test section of rope was cut from the center of the 30 cm

rope without removing the rope from the interior surface of the pouch. One end of the test section was then grasped between the user's thumb and forefinger, and slowly pulled free from the surface of the pouch at an angle of about 90° until the other end of the rope released from the pouch such that the entire test section was 5 suspended vertically above the opened pouch. The total pull time was about 3 seconds. The length of the test section was then measured and the stretch recorded as the extent to which the length exceeded the original 15cm. A sample was said to pass the stretch test if the stretch was no greater than about 50mm.

10 D. Tack

The pouch containing the rope was opened and a 15 cm section of the rope was then cut and laid gently in a substantially circular loop on the surface of a cold rolled steel test panel measuring 10 cm x 15 cm (available from ACT of Hillside, MI) which had previously been wiped clean with toluene. Care was taken 15 not to press the rope into the surface of the steel test panel. The panel was then inverted and the amount of time that elapsed before the loop fell off the test panel was measured. A composition was said to pass the tack test if it did not fall off the test panel after a period of 30 seconds.

20 E. End Seal

The pouch containing the rope was opened and a 15 cm section of the rope was then cut and laid gently in a substantially circular loop on the surface of a cold rolled steel test panel measuring 10 cm x 15 cm (available from ACT of Hillside, MI) which had previously been wiped clean with toluene. Care was taken 25 not to press the rope into the surface of the steel test panel. The ends of the loop were lifted from the steel panel and overlapped with each other to create an overlap joint measuring approximately 3 mm. The overlap joint thus created was then pressed back onto the steel surface using moderate thumb pressure. Next, the loop was lifted from the surface of the steel panel by grasping two portions of the 30 loop located on opposite sides of the loop about 5cm from the overlap joint. A

sample was said to pass the end seal test if the joint did not pull-apart during the lifting process.

**F. Shear Adhesion**

5 Unpolished, cold-rolled steel strips measuring 76 mm x 25 mm x 1 mm were cut from panels commercially available from ACT of Hillsdale, MI. Sealant was applied full-width to the end of a test strip. Bond thickness was controlled to 500 micrometers by placing wire segments of appropriate diameter in the sealant. The end of a second steel strip was placed over the sealant, and the extent of strip 10 overlap adjusted to 12.7 mm using a ruler. Excess sealant was removed from the bonded test strips, leaving a adhesively bonded region between the strips measuring 25 mm x 12.7 mm x 0.5 mm. The test specimens thus produced were then cured for 7 days at 25°C/50 % relative humidity. Following cure, the tab ends of the test specimens were clamped into the jaws of a Sintech 6W tensile test system 15 (available from MTS Systems Corp. of Research Triangle Park, NC), and the specimens were pulled at a cross-head speed of 5 centimeters per minute. The shear adhesion at break was recorded.

**G. Durometer**

20 Uncured sealant was sandwiched between two suitable liners (such as low density polyethylene and the like) and pressed to a thickness of 2 mm. The pressed sealant was then cured for 7 days at 25°C/50% relative humidity and cut into test specimens measuring 50 mm x 25 mm x 2 mm after which the durometer (Shore A hardness) of the cured samples (stacked three together) was measured 25 according to ASTM D-2240.

**H. Immersion Test No. 1**

A cure sample was immersed in ASTM #3 oil (available from R.E. Carroll, Inc. of Trenton NJ) at 150°C for 70 hours, after which tensile strength, 30 elongation, and Shore A hardness were measured.

I. Immersion Test No. 2

A cured sample was immersed in motor oil (Amoco SAE 10W30 motor oil available from Amoco Corp.) at 150°C for 14 days, after which the tensile strength, elongation, and Shore A hardness were measured.

J. Immersion Test No. 3

A cured sample was immersed in a 50/50 weight percent mixture of ethylene glycol/water at 121 °C for 14 days, after which the tensile strength, elongation, and Shore A hardness were measured.

**Example 1**

Example 1 shows the preparation of various partially chain extended silicone-oligoureas.

Polydiorganosiloxane oligourea segmented copolymer Sample 1 was prepared by dissolving 105.5 grams silicone diamine having a molecular weight of 5,280, in 80 grams toluene. To the solution was added, in a dropwise fashion, a mixture of 3.25 grams TMXDI (13.3 millimoles, or mmoles) and 3.93 grams (13.3 mmoles) of octadecyl isocyanate in 17 grams toluene at room temperature. The resulting polydiorganosiloxane oligourea segmented copolymer was air dried.

Polydiorganosiloxane oligourea segmented copolymer Sample 2 was prepared by dissolving 105.5 grams silicone diamine having a molecular weight of 5,280, in 80 grams toluene. To the solution was added, in a dropwise fashion, a mixture of 3.25 grams TMXDI (13.3 mmoles) and 1.58 grams (13.3 mmoles) of phenyl isocyanate in 17 grams toluene at room temperature. The resulting polydiorganosiloxane oligourea segmented copolymer was air dried.

Polydiorganosiloxane oligourea segmented copolymer Sample 3 was prepared by dissolving 79 grams (8.0 mmoles) of the silicone-monoamine having a MW-9,800, 21 grams (4.0 mmoles ) of silicone diamine having a MW = 5,280, in 69 parts toluene. Then 1.96 parts (8.0 mmoles ) of tetramethyl-*m*-xylylene diisocyanate, in 40 parts toluene was added dropwise under agitation at room

temperature. The resulting polydiorganosiloxane oligourea segmented copolymer was air dried.

Polydiorganosiloxane oligourea segmented copolymer Sample 4 was prepared by dissolving 100 grams silicone diamine having a molecular weight of 5 22,300, (4.45 mmoles) in 50 grams toluene. To the solution was added, in a dropwise fashion, a mixture of 0.75 grams (2.99 mmoles) 1,12-dodecane diisocyanate and 0.46 grams (2.99 mmoles) of IEM in 20 grams toluene at room temperature. The resulting polydiorganosiloxane oligourea segmented copolymer was air dried.

10 Polydiorganosiloxane oligourea segmented copolymer Sample 5 was prepared as described in Sample 2, with the exception that 3.35 grams of 1,12 dodecane diisocyanate was substituted for TMXDI.

15 Polydiorganosiloxane oligourea segmented copolymer Sample 6 was prepared as described in Sample 5, with the exception that 3.93 grams (13.3 mmoles) of octadecyl isocyanate was substituted for phenyl isocyanate.

Polydiorganosiloxane oligourea segmented copolymer Sample 7 was prepared by dissolving 100 grams silicone diamine having a molecular weight of 38,600, (2.58 mmoles) in 50 grams toluene. To the solution was added, in a dropwise fashion, a mixture of 0.43 grams (1.73 mmoles) 1,12-dodecane diisocyanate, and 0.27 grams (1.73 mmoles) IEM in 20 grams toluene at room 20 temperature. The resulting polydiorganosiloxane oligourea segmented copolymer was air dried.

The polydiorganosiloxane oligourea segmented copolymer Sample 8 was prepared as in Sample 3, except that 1.98 parts (7.9 mmoles) of 1,12- 25 dodecane diisocyanate was substituted for the tetramethyl-*m*-xylylene diisocyanate.

Polydiorganosiloxane oligourea segmented copolymer Samples 1 through 8 are listed in Table 1.

Table 1

Sample	Silicone (MW)	Di-isocyanate	Mono-isocyanate	degree of polymerization (DP)
1	5,280	TMXDI	Octadecyl	3
2	5,280	TMXDI	Phenyl-NCO	3
3	Trimer 1	TMXDI	None	3
4	22,300	1,12-ddDI	IEM	3
5	5,280	1,12-ddDI	Phenyl-NCO	3
6	5,280	1,12-ddDI	ODI	3
7	38,600	1,12-ddDI	IEM	3
8	Dimer 1	1,12-ddDI	None	2

Trimer 1 consisted of two, 9,800 MW polydimethylsiloxane monoamine units and one 5,000 MW interconnected with two urea linkages formed from TMXDI.

5 Dimer 1 consisted of two 9,800 polydiorganosiloxane monoamine units connected to two urea linkages formed from 1,12-dodecane diisocyanate.

One gram of polydimethylsiloxane polyurea copolymer Samples 1-8 were dissolved in 5 grams of toluene. When dissolution of the copolymer was complete, 9 grams of Masil™ SRF 150,000, hydroxy-terminated PDMS was added 10 and mixed into the copolymer solution until thoroughly dissolved. The toluene was evaporated to yield a polymeric composition.

### Example 2

This example describes the preparation of various polymeric 15 compositions according to the invention using an extruder. The following equipment and method were used to prepare the polymeric compositions of the present invention.

#### General Extrusion Procedure

20 The compositions were made using a Berstorff 40 millimeter diameter 1600 millimeter length co-rotating twin screw extruder equipped with double-start, intermeshing screws. The extruder barrel was divided into ten zones. Zone 1 contained the primary feed port and was located the furthest from the exit die. Attached to the feed port was a split-plate feed hopper which kept powders and

liquids from mixing prematurely and clogging the feed port. Screw speeds ranged from 100 to 200 revolutions per minute (RPM). To ensure smooth, continuous delivery, diisocyanate was metered into the silicone fluid feed stream ahead of the point where the silicone fluid feed stream entered the extruder. The diisocyanate 5 silicone fluid dispersion, the silicone-diamine, and optional powders, were delivered to the extruder through the feed-hopper in zone 1. To prevent premature reaction, the silicone-diamine was fed to the feed hopper through a separate line. Barrel temperatures were set below room temperature to minimize reaction of vinyl oximinosilane (crosslinker) and aminosilane (adhesion promoter). Generally, 10 as a series of experiments proceeded, the actual barrel temperature slowly changed toward a steady state point that was a function of the variables of each individual experiment and of distance along the barrel length. Actual barrel temperatures ranged from about 25°C to over 100°C. The crosslinker and adhesion promoter were premixed and metered into the process stream in zone 8. The overall flow 15 rate ranged from 40 to 70 grams per minute.

The resultant rheology-modified silicone compositions were extruded through a die having a circular opening to produce a clear to translucent thickened gel. Exceptions to this general procedure are noted in the numbered examples.

In Example 2, the flow rates of components to the extruder were 20 adjusted to yield compositions having the following weight percentages: 75.5 % Masil™ SFR 150,000 silicone fluid, and 24.5 % silicone-polyurea copolymers. The NCO/NH<sub>2</sub> ratios were varied by adjusting the flow rate of H<sub>12</sub>MDI. Polydiorganosiloxane diamine having a MW of 16,700 was used in all runs. Shear modulus measurements were made on the uncured compositions using the test 25 procedures described above.

Table 2

Sample	NCO/NH <sub>2</sub> Ratio	Viscosity at 0.1 rad/sec (Pa.s)	Viscosity at 1 rad/sec (Pa.s)	Complex Shear Modulus (kilopascals) (kPa)			
				0.1 radians per second		100 radians per second	
				Storage Mod.	Loss Mod	Storage Mod.	Loss Mod
9	1.03	28,430	3,810	2.79	0.530	18.0	16.1
10	1.07	27,550	4,250	2.60	0.898	19.5	17.1
11	1.10	40,530	8,180	3.52	2.010	37.4	22.9
12	1.11	30,800	4,640	2.92	0.966	19.5	16.2
13	1.15	31,370	2,570	3.01	0.885	18.2	15.6
14	1.20	28,070	5,084	2.48	1.325	21.9	17.7

The data of Table 2 shows there is a NCO/NH<sub>2</sub> ratio beyond 1:1 that produces maximum chain extension (as determined by viscosity and shear modulus measurements made at 0.1 radians per second) for mixtures of silicone fluids containing silicone-polyurea segmented copolymer.

#### Example 3 (Moisture curable Pressure-Sensitive Adhesive)

A homogeneous mixture consisting of 8.0 grams of PPG SFR-2000 hydroxy-terminated PDMS and 2.0 grams of silicone-diamine MW = 20,171 was prepared. Next 0.02 grams of H<sub>12</sub>MDI was added and the viscosity rose slightly. After 10 minutes of mixing, 1.0 gram of vinyl oximino silane (VOS) (Allied-Signal OS-2000) was added. After incorporation of the VOS, 16.0 grams of GE SR-545, MQ Resin 60% in toluene (available from General Electric) was added and the resulting viscous mixture knife coated onto poly(ethylene terephthalate) (PET) to produce a dry film thickness of about 40 micrometers. The coating was allowed to dry and moisture cure in air for 72 hours. The resulting pressure-sensitive adhesive film was tacky to touch and had a 180 peel adhesion of 39.4 Newtons per decimeter (average of two (2) tests) when pulled from a glass substrate at a rate of 230 centimeters per minute.

#### Example 4

This example shows the effect of increasing the concentration of silicone-urea copolymer on the viscosity and tensile properties of the compositions.

The General Extrusion Procedure from Example 2 was used to produce samples 15 to 23, as described in Table 3. The flow rates of components to 5 extruder were adjusted to yield compositions having the weight percentages shown in Table 3. To achieve these compositions, the overall flow rate ranged from about 9 to 225 grams per minute. The silicone fluid was Masil™ SFR 150,000. The silicone-diamine was prepared as described by the above general procedure, and had a molecular weight of 16,700. The diisocyanate was Desmodur W (H<sub>12</sub>MDI), 10 and the moisture crosslinker was vinyl oximino silane (OS-2000). The NCO/NH<sub>2</sub> ratio was maintained at 1.10 for all runs. As the concentration of copolymer in the composition was increased it was necessary to increase the temperature in the extruder barrel as shown in Table 3. No tensile data is provided for compositions 15 without crosslinker. Shear modulus measurements were made on uncured samples of the composition as described above.

Table 3

Sample	Silicone Fluid (wt %)	silicone polyurea copolymer (wt %)	Moisture Crosslinker (wt %)	Temp. (C)	Tensile (kPa)	Elong. (%)	Complex Shear Modulus (kilopascals kPa)		
							0.1 radians per second	1 radians per second	100 radians per second
15	97.3	2.7	0	28	n/a	n/a			
16	93.4	2.6	4.0	33	385	291			
17	90.0	10	0	38	n/a	n/a			
18	86.6	9.5	3.9	40	435	353			
19	59.8	40.2	0	81	n/a	n/a			
20	57.3	38.6	4.1	79	475	484	0.229	0.564	1.40
21	39.8	60.2	0	106	n/a	n/a	34.3	9.91	50.2
22	38.2	57.8	4.0	95	455	589	9.71	8.65	24.3
23	30.3	69.7	0	174	n/a	n/a	117	13.1	136
									182
									195

**Example 5**

This example shows how changing the isocyanate used to form the silicone-polyurea copolymer segments affects the viscosity and tensile properties of the composition.

5        The General Extrusion Procedure of Example 2 was used to produce the samples described in Table 4. The flow rates of components to extruder were adjusted to yield compositions having the following weight percentage: 71.5 % Masil™ SFR 150,000 silicone fluid, 24.5 % silicone-polyurea copolymer, and 4.0 % moisture crosslinker vinyl oximino silane (OS-2000). The polydiorganosiloxane  
10      polyurea segmented copolymer was made in the extruder by reacting silicone-diamine of molecular weight 16,700 prepared as described above, using the diisocyanates and NCO/NH<sub>2</sub> ratios shown in Table 4. Samples of compositions containing crosslinker were moisture cured. No tensile data is provided for compositions without crosslinker.

15

Table 4

Sample	NCO type	NCO/NH <sub>2</sub> ratio	Temp. °C	Tensile (kPa)	Elong. (%)	Complex Shear Modulus (kilopascals kPa)					
						0.1 radians per second		1 radian per second		100 radians per second	
						Storage Mod.	Loss Mod.	Storage Mod.	Loss Mod.	Storage Mod.	Loss Mod.
24	Isonate 2143L	1.05	119	400	284			2.02	1.20	15.2	15.0
25	IPDI	1.05	79	385	347	2.01	1.51	4.32	3.09	24.2	17.0
26	TMXDI	1.10	80	360	222			1.49	1.10	16.0	17.7

**Example 6**

This example illustrates the preparation of a polymeric composition using a silicone-polyurea copolymer which in turn was prepared using a silicone diamine having a molecular weight of 5,350.

5        The General Extrusion Procedure described in Example 2 was used to prepare the Samples described in Table 5. The flow rates of components to extruder were adjusted to yield compositions having the following weight percentage: 71.5 % Masi<sup>TM</sup> SFR 150,000 silicone fluid, 24.5 % silicone-polyurea copolymer, and 4.0 % moisture crosslinker vinyl oximino silane (OS-2000). The  
10      silicone-urea copolymer was made in the extruder by reacting silicone-diamine having a molecular weight of 5,350, and using the diisocyanate and NCO/NH<sub>2</sub> ratio shown in Table 5. The of composition was cured and tested for tensile properties. Shear modulus measurements were made on the uncured sample of the composition as described above.

Table 5

Sample	NCO/NH <sub>2</sub> ratio	Temp (C)	Tensile (kPa)	Elong. (%)	Complex Shear Modulus (kilopascals kPa)			
					0.1 radian per second	1 radian per second	100 radians per second	
					Storage Mod.	Loss Mod.	Storage Mod.	Loss Mod.
27	1.05	25	370	206	0.158	1.11	1.90	7.02
							96.7	72.6

**Example 7**

This example shows that pre-formed polydimethylsiloxane polyurea segmented copolymer can be combined with silicone fluids in the extruder to 5 produce the compositions of the invention.

Polydimethylsiloxane polyurea segmented copolymer containing no silicone fluid was prepared from a polydimethylsiloxane diamine having a number average molecular weight of 5,350, and Desmodur W at an NCO:NH<sub>2</sub> ratio of 1:1, using a solventless continuous extrusion process. The polydimethylsiloxane 10 diamine was injected into zone 8 of the 40 mm Berstorff co-rotating extruder of Example 2. The diisocyanate was injected into zone 9 with the screws rotating at 100 revolutions per minute. The temperatures of the individual zones were: zones 1 through 7 (not used); zone 8 - 60°C; zone 9 - 120°C, zone 10 and endcap - 180°C. The resulting polydimethylsiloxane polyurea segmented copolymer was 15 extruded into a strand, cooled in a liquid bath, and pelletized.

The general procedure described in Example 2 for preparing polydimethylsiloxane polyurea segmented copolymer / silicone fluid blends was modified as follows. The pelletized polydimethylsiloxane polyurea segmented copolymer prepared above was fed into zone 1. The screw speed was 30 20 revolutions per minute and the temperature of zones 2 through 6 were maintained at 190°C to melt the copolymer. Hydroxy-terminated polydimethylsiloxane (Masil™ SFR 150,000) was added through a feed port in zone 6 at 44.3 g/min. The temperature in zone 7 was maintained at 160°C. Four weight percent VOS 25 moisture crosslinker (OS-2000) was added into zone 8. Zones 8 through 10 and endcap were set at 180°C. The flowrates of the components were adjusted accordingly to yield the compositions displayed in Table 6. The extrudate contained a very small fraction of polydimethylsiloxane polyurea segmented copolymer that had not completely blended with the silicone oil, due to incomplete melting. However, the effect of the segmented copolymer on the extrudate was 30 apparent, as it displayed high viscosity and excellent elongation properties. Shear

modulus measurements were performed on uncured samples. Samples of the composition were moisture cured and tested for tensile properties.

Table 6

Sample	silicone polyurea (wt %)	silicone fluid (wt %)	Temp. @ Exit die, C	Tensile (kPa)	Elong. (%)	Complex Shear Modulus (kilopascals kPa)		
						0.1 radian per second	100 radians per second	
						Storage Mod.	Loss Mod.	Storage Mod.
								Loss Mod.
28	23.9	72.1	105	495	294	1.84	1.31	25.3
29	17.4	78.5	82	370	278.	2.54	1.28	24.0
								19.7

**Example 8**

This example shows the production of a curable self-supporting sealant rope using a high molecular weight silicone diamine. The General Extrusion Procedure described in Example 2 was used to produce Sample 30 described in

5 **Table 7.**

**Table 7**

<b>Sample</b>	<b>30</b>
Silicone diamine MW	105,000
NCO/NH <sub>2</sub> ratio (H12MDI)	1.05
Silicone polyurea (%)	20%
vinyl oximino silane (%)	3.6%
Adhesion promoter (%) and type from OSi Specialties	0.9% A1120
Fumed silica (%) (Degussa R974V)	15%
PPG Masil SFR 150,000	60.5
<b>PROPERTIES</b>	
Viscosity (Pascal seconds) @ 0.1 radians per second	9.39 x 10 <sup>4</sup>
Tensile (kPa)	1780
Elongation (%)	494 %
Lap shear adhesion (kPa)	1815
Storage Mod. (0.1 rad./sec.)(kPa)	8.28
Loss Mod. (0.1 rad./sec.)(kPa)	4.43
Storage Mod. (100 rad./sec.)(kPa)	62.8
Loss Mod. (100 rad./sec.)(kPa)	44.1

**10 Example 9**

This example describes the preparation of a composition according to the invention that is useful as a sealant, e.g., in an automobile engine. The composition was prepared using a 25 mm co-rotating, fully intermeshing Berstorff Extruder having a L/D of 29.5. All liquid components were fed into zone 1 of the 15 extruder, while the solids (stream 3) were fed into zone 3. The composition of the feed streams was as follows:

Table 8

Feed Stream	Component	Wt. %
1	Masil SFR 150,000 Silanol terminated polydimethylsiloxane	55
2	50/50 = GE SR545/SFR 18,000 (solvent was stripped) (MQ resin + Silanol terminated polydimethylsiloxane)	5
3	Aerosil R974V (Dense hydrophobic fumed silica)	15
4	22,000 molecular weight silicone diamine	20
5	Silane mixture (7:1 = Allied-Signal vinyl oximino silane: OSi Y11597)	5
6	Dicyclohexymethane-4,4' - Diisocyanate (Desmodur W, Miles Inc.)	0.242

The reaction product was tested according to the test procedures described above, and the results are given in Tables 9 through 11 below.

5

Table 9

	Initial	Immersion Test #1	Immersion Test #2	Immersion Test #3
Tensile (kPa)	3075	1710	655	1730
Elongation	547%	560%	738%	757%
Durometer (Shore A)	37	33	25	40
Shear Adhesion (kPa)	495			

Table 10

Uncured Handling	
Tack	Pass
Stretch	Pass
End Seal	Pass

10

Table 11

Radians Per Second	Complex Shear Modulus (kPa)	
	Storage Modulus	Loss Modulus
1	299	52.5
100	493	115

**Example 10**

A copolymer was produced by feeding polydimethylsiloxane diamine having a molecular weight 22,300 into the first zone of an 18 mm co-rotating twin screw extruder having a 40:1 length:diameter ratio (available from Leistritz Corporation, Allendale, NJ) at a rate of 6.22 g/min (0.000558 equivalents amine/min). A mixture of 33.3 parts by weight tetramethyl-m-xylylene diisocyanate, 21.1 parts by weight isocyanatoethyl methacrylate, and 45.6 parts by weight DAROCUR™ 1173 was fed into the sixth zone at a rate of 0.134 g/min (0.000549 equivalents isocyanate/min). The feed line of this stream was placed close to the screw threads. The extruder had double-start fully intermeshing screws throughout the entire length of the barrel, rotating at 50 revolutions per minute. The temperature profile for each of the 90 mm long zones was: zones 1 through 4 - 30°C; zone 5 - 40°C; zone 6 - 60°C; zone 7 - 90°C; zone 8 and endcap - 120°C.

6.04 grams of the above-described copolymer was mixed with 26.32 grams of Goldschmidt TEGO RC-726 and 30 grams of dichloromethane for about 1.5 hours. Next 3.58 grams of Darocur™ 1173 photoinitiator (available from Ciba-Geigy, Hawthorne, NY) was added and mixed. The solution was cast and air dried on a UV transparent liner under subdued light and stored in the dark. The mixture dried to a very thick oil, which upon exposure to UV light cured to rigid film.

20

**Example 11**

In Example 11, a silicone polyurea copolymer was made as follows: silicone diamine having a molecular weight of 35,700 was injected at a rate of 38.8 grams per minute into the third zone of a co-rotating twin screw Werner-Pfleiderer extruder, having 1350 millimeter length, 30 millimeter diameter. H<sub>12</sub>MDI Desmodur W was fed into the extruder at zone 6, at a rate of 0.290 g/min. All screws were fully intermeshing double-start screws, and the rotational speed was 200 revolutions per minute. The temperature profile of each of the 90 millimeter zones was: zones 1 through 3 - 50°C; zones 4 through 6 - 60°C; zones 7 and 8 - 115°C; zones 9 through 13 - 170°C; zone 14 - 180°C; and zone 15 - 151°C. Vacuum was pulled on zone 13.

A tackified curable composition was prepared by mixing 30 grams of a silicone terminated with acrylamidoamido groups, molecular weight 35,000, made as described in US Patent 5,091,483, 10 grams of the above-described silicone polyurea copolymer, and 50 grams toluene. 40 grams MQ resin powder (GE 5 Silicones 1170-002) and 0.4 grams Darocure™ 1173 photoinitiator were added, and the mixture was agitated until it formed a homogeneous solution. The solution was poured onto a release liner and dried in air. A portion of this dried composition was coated with a heated knife coater at 100°C between a 1.5 mil primed polyester film and a release liner, to a thickness of 75 µm, and cured by exposure to low 10 intensity UV lights for 20 minutes. The resulting pressure-sensitive adhesive coating was tested for 180° peel strength from glass. The result was a 180° peel strength from glass value of 51.9 N/dm (Newtons per decimeter).

### Glossary

15

Ingredient	Supplier
Masil™ SFR 150,000	PPG Industries, Inc., Pittsburgh, PA
Masil™ SFR 80,000	PPG Industries, Inc., Pittsburgh, PA
Masil™ SFR 2,000	PPG Industries, Inc., Pittsburgh, PA
Masil™ SFR 18,000	PPG Industries, Inc., Pittsburgh, PA
OS-2000 vinyl aximino silane	Allied-Signal, Morristown, NJ
N-beta-((aminoethyl) -gamma-aminopropyl trimethoxy silane (A1120)	OSi Chemicals, Danbury, CT
gamma-ureidopropyl trimethoxysilane (Y11542)	OSi Chemicals, Danbury, CT
(Y11597) isocyanurate trimethoxy silane	OSi Chemicals, Danbury, CT
Aerosil™ R974 fume silica	Degussa Corp., Dublin, OH
methyleneidiphenylene-4,4'-diisocyanate (H <sub>12</sub> MDI)	Bayer, Pittsburgh, PA
tetramethyl- <i>m</i> -xylylene diisocyanate (TMXDI)	Cytek Ind. Inc., West Paterson, NJ
1,12-diisocyanatododecane (1,12-ddDI)	Aldrich Chemical, Milwaukee, WI
ISONATE™ 2143L	Dow Chemical Co., Midland, MI
SR-545 MQ resin	General Electric Co., Waterford, NY

**What is claimed is:**

1. **A composition comprising:**
  - (a) **a silicone fluid;**
  - (b) **a silicone-urea segmented copolymer; and**
  - 5 (c) **no more than about 30% by weight of a silicate resin.**
2. **A composition according to claim 1 comprising at least about 30% by weight of said silicone fluid and up to about 70% by weight of said silicone-urea copolymer.**
- 10
3. **A composition according to claim 1 wherein said silicone fluid comprises a substantially non-curable silicone fluid.**
- 15
4. **A composition according to claim 1 wherein said silicone fluid comprises a curable silicone fluid.**
5. **A composition according to claim 1 wherein said silicone-urea copolymer comprises a polydiorganosiloxane-polyurea segmented copolymer having a degree of polymerization of at least 10.**
- 20
6. **A composition according to claim 1 comprising up to about 25% by weight of said silicone-urea copolymer.**
- 25
7. **A composition comprising:**
  - (a) **a silicone fluid; and**
  - (b) **a silicone-urea segmented copolymer comprising a polydiorganosiloxane-oligourethane segmented copolymer having terminal groups selected from the group consisting of functional end groups and non-functional end groups, and a degree of polymerization less than 10.**
- 30

8. A composition according to claim 7 comprising at least about 30% by weight of said silicone fluid and up to about 70% by weight of said silicone-urea copolymer.

5 9. A composition according to claim 7 wherein said silicone fluid comprises a substantially non-curable silicone fluid.

10. A composition according to claim 7 wherein said silicone fluid comprises a curable silicone fluid.

10

11. A composition according to claim 7 comprising up to about 25% by weight of said silicone-urea copolymer.

12. A curable composition comprising a curable silicone fluid and a 15 silicone-urea segmented copolymer.

13. A method for preparing a polymeric composition comprising the steps of:

20 providing a reaction mixture comprising a polyisocyanate, a polydiorganosiloxane diamine, and a silicone fluid; and reacting said polyisocyanate and said diamine with each other in the presence of said silicone fluid to produce a polymeric composition comprising said silicone fluid and a silicone-urea segmented copolymer.

25 14. A method according to claim 13 wherein said reaction mixture is substantially solvent-free.

15. A method according to claim 13 wherein said reaction mixture further comprises a silicate resin.

30

16. A method for preparing a polymeric composition comprising the steps of:

reacting a polyisocyanate and a polydiorganosiloxane diamine in the absence of solvent to form a silicone-urea segmented copolymer; and

5 combining said copolymer with a silicone fluid to form said polymeric composition.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 96/14028

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08L 83/10, C08G 18/61 // C09J 183/10  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08G, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A1, 0667382 (DOW CORNING CORPORATION), 16 August 1995 (16.08.95), claims 1,4-7, abstract --	1-16
A	EP, A2, 0250248 (MINNESOTA MINING AND MANUFACTURING COMPANY), 23 December 1987 (23.12.87), claims 1-14, abstract --	1-16
A	EP, A2, 0380236 (MINNESOTA MINING AND MANUFACTURING COMPANY), 1 August 1990 (01.08.90), claims 1-2, abstract -----	1-16

Further documents are listed in the continuation of Box C.  See patent family annex.

- \* Special categories of cited documents
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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/ European Patent Office, P.O. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  BARRRO NILSSON

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.

PCT/US 96/14028

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A1- 0667382	16/08/95	CA-A- JP-A-	2141651 7252463	10/08/95 03/10/95
EP-A2- 0250248	23/12/87	AU-B- AU-A- EP-A- JP-A- JP-A- US-A- US-A- US-A- US-A-	591989 7447487 0737700 8231726 63003029 5214119 5290615 5461134 5512650	21/12/89 24/12/87 16/10/96 10/09/96 08/01/88 25/05/93 01/03/94 24/10/95 30/04/96
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